

A New Study of the Acid Rhodo Complex Salt $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$ Shows That the Crystals are Orthorhombic

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Abstract

Diffraction data recorded at low temperature with Mo $K\alpha$ from two different crystals have been used in the refinement of the structure of the acid rhodo complex salt, μ -hydroxo-bis[pentaamminechromium(III)] chloride monohydrate $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$. Several structural models in two different tetragonal space groups have been investigated before a satisfactory description of the structure was obtained. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 16.155(3)$, $b = 16.154(3)$, $c = 14.750(7)$ Å and $Z = 8$. The apparent tetragonal symmetry arises due to rotation twinning of the crystals. The diffraction pattern is further complicated by tetragonal pseudo-symmetry of the chromium sites, which means that reflections with $l = 2n + 1$ are systematically weak. The two independent dimeric cations are involved in slightly different hydrogen-bond patterns. This observation and the relative orientation of the dimers in the crystal is in accordance with spectral and magnetic measurements.

1. Introduction

The compound known as the acid rhodo is a classical dimeric chromium(III) complex first reported by Jørgensen (1882), who studied its acid/base properties. It has been studied extensively since. Its constitution was correctly described by Werner (1914), as two $[\text{Cr}(\text{NH}_3)_5]^{3+}$ moieties linked by a μ -hydroxo group.

The acidic and basic complexes containing single hydroxo- or oxo-bridged chromium(III) ions have been shown to be exchange coupled, with a super-exchange of the chromium ions through the bridging groups. These complexes have therefore been considered as valuable intermediates between magnetically dilute compounds and ferromagnetic and antiferromagnetic compounds. As such they have attracted much interest. The exchange interactions appear to be affected by the nature of the bridge, the Cr—O—Cr angle, the counter ions and the degree of hydration (Earnshaw & Lewis, 1961; Schäffer,

1958; Wilmarth, Graff & Gustin, 1956; Kobayashi, Haseda & Mori, 1965). This may be exemplified by the difference in magnetic properties between the basic (oxo bridged) and the acid rhodo chloride complexes. For the acid rhodo complex only a small interaction between the two magnetic chromium ions through the hydroxo bridge has been observed. For the basic rhodo complex, however, a pronounced magnetic interaction has been observed, associated with an increase of π -bonding between the magnetic chromium ions and the bridging oxygen. This is mainly due to the shorter Cr—O distance in the basic rhodo complex.

Two different modifications of the acid rhodo chromium(III) chloride complex have been characterized: a monohydrate and a dihydrate; the suggested trihydrate by Linhard & Weigel (1959) appears to be identical to the dihydrate (Engel & Güdel, 1977). The dihydrated compound shows a good agreement between results obtained by different techniques, and its spectroscopic and magnetic properties may be explained by the crystal structure (Ferguson & Güdel, 1973; Engel & Güdel, 1977). The structure of the monohydrated compound (hereafter denoted the acid rhodo complex) is much more speculative. It has been studied by spectroscopic and magnetic methods and the interpretation of these measurements has been hampered because the spectroscopic results disagree with the reported crystal structures of the acid rhodo complex.

Studies of the monohydrated acid rhodo complex by polarized absorption spectroscopy and measurements of the Zeeman effect by Riesen & Güdel (1986) clearly show that two non-equivalent dimer sites are present. They also suggest that the Cr—O—Cr planes of the two independent dimers are tilted approximately 90° with respect to each other.

The first crystallographic work on the acid rhodo complex was performed by Urushiyama, Nomura & Nakahara (1970), who reported that the crystals belong to the tetragonal space group $P4_12_12$ with $a = 16.26$, $c = 14.80$ Å. This model has two half molecules in the asymmetric unit and two crystallographically different bridging O atoms placed on the twofold rotation axis. They refined the structure to $R(F) = 0.16$ using 1169

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reflections; although they did not publish any atomic coordinates, they reported the Cr—O—Cr angle 154°, the Cr—O distance 2.00 Å and the average Cr—N distance 2.07 Å. Shortly after, Veal *et al.* (1973) published a more detailed structural description in space group $P4_2/mnm$, $a = 16.259$, $c = 7.411$ Å. Using 228 reflections they obtained $R(F) = 0.077$. In their description the dimeric complex is found at a crystallographic mirror plane. The Cr—O—Cr angle was found to be 166° and the Cr—O distance was 1.94 Å. The N atom *trans* to the bridging oxygen showed a Cr—N distance of 2.15 Å, the other N atoms showed an average Cr—N distance of 2.08 Å. The high atomic displacement parameters of this model indicated a disorder of the chloride ions and of the water O atoms, leaving the impression that the structure was not satisfactorily described. This model has a quarter of a dimer per asymmetric unit and is, therefore, at variance with the results from spectroscopic measurements, which indicate two dimers per asymmetric unit.

In an era where structure determinations for small molecules are often considered to be a routine job we found it challenging that a compound so extensively studied as the acid rhodo chloride monohydrate obviously did not have its structure correctly reported in the literature. This initiated the present investigation.

2. Experimental

2.1. Preparation

The complex was synthesized as described in the literature (Linhard & Weigel, 1959). A slightly HCl acidic saturated solution of the title complex salt was placed in a desiccator in the dark for several days. The needles thus obtained were separated from the mother liquor and dried with paper tissue. They cleave easily perpendicular to the needle axis. The crystals have a beautiful dark red colour and the individual crystals tend to grow together along the needle axis.

2.2. X-ray data collection

Several crystals were examined on a Weissenberg camera and one was selected for data collection. After the structure was finally solved several years later we realized that we needed a more elaborate data set and a second crystal from a new batch was used.

A CAD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation was used for both data collections. The first crystal was cooled to 110.0 (5) K during data collection with an Enraf–Nonius gas-flow low-temperature device. For the second crystal the data collection was performed in two different periods and the crystal was cooled to 122.0 (5) K with an Enraf–Nonius gas-flow low-temperature device during the first period and with an Oxford Cryosystems Cryostream during the second period.

The unit-cell parameters of crystal (1) listed in Table 1 were determined from a least-squares refinement of the setting angles for 18 reflections ($19 < \theta < 23^\circ$). Weissenberg films had shown that all reflections having $l = 2n + 1$ were systematically weak. Therefore, we took special care and measured these in a separate data collection with a fixed scan velocity of $0.69^\circ \text{ min}^{-1}$. We used the prescan mode for the $l = 2n$ reflections of crystal (1) so that weak reflections were measured only in the fast scan mode. It has been shown that such prescanned reflections bias the intensity distribution (Seiler, Schweizer & Dunitz, 1984) and they were therefore removed from the data set. For crystal (2) the data collection was performed with the prescan mode suppressed. The intensities of three standard reflections were measured every 10^4 s and the orientation of the crystal was checked every 300 reflections.

As seen from Table 1, reflections ($h, k, \pm l$) were collected to $2\theta = 82^\circ$ for crystal (1). This would normally be considered sufficient for the refinement of the crystal structures that belong to a tetragonal or orthorhombic space group. During structure refinement, however, twinning of the crystal was encountered and to be able to describe this properly a new data collection was performed on a second crystal (2) and a full sphere of reflections was collected to $2\theta = 32^\circ$. It was subsequently realized that higher resolution data were desirable and a data collection for a full sphere to $2\theta = 50^\circ$ was initiated. Unfortunately, during this second experiment, the cooling system failed, and the crystal was heated and destroyed. At this stage, however, we had managed to measure half a sphere of data, *i.e.* ($h, \pm k, \pm l$), to $2\theta = 50^\circ$, which could be supplemented with a full sphere of data to $2\theta = 32^\circ$. We decided that this was more than sufficient to refine the structure satisfactorily. Therefore, only the data from crystal (2) were used for the final structure refinement and description.

3. Results

3.1. Analysis of diffraction data

Data reduction was performed with the *DREADD* program package (Blessing, 1987). It included corrections for Lorentz, polarization and background effects. The data of crystal (1) were rescaled by a third-order polynomial fit according to the small decrease in the intensities of the standard reflections. A Gaussian absorption correction with grid size $8 \times 16 \times 32$ was applied to the data for crystal (2) (transmission factors varied between 0.70 and 0.88).

All strong reflections could be indexed in a tetragonal cell with $a \simeq 16.16$ and $c \simeq 7.38$ Å. However, very weak reflections were definitely present in-between, so that the true cell has $a \simeq 16.16$ and $c \simeq 14.75$ Å. Analysis of the data showed that reflections fulfilling ($h00$, $h = 2n + 1$;

Table 1. Data collection summary

	(1)	(2a)	(2b)
Crystal			
<i>a</i> (Å)	16.157 (4)	16.155 (3)	16.164 (5)
<i>b</i> (Å)	16.164 (5)	16.154 (3)	16.166 (3)
<i>c</i> (Å)	14.766 (3)	14.750(7)	14.768 (4)
<i>V</i> (Å ³)	3856 (2)	3849 (2)	3858 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.832	1.835	1.831
Temperature (K)	110.0 (5)	122.0 (5)	122.0 (5)
No. of reflections used for cell	18	18	18
Crystal size (mm ³)	0.175 × 0.275 × 0.45		0.07 × 0.18 × 0.55
<i>T</i> _{min}		0.72	0.70
<i>T</i> _{max}		0.88	0.88
θ range for data collection (°)	1.78–40.96	1.97–16.21	1.97–25.21
Standard reflections	3	3	5
Variation (%)	13.5	3	2.5
Scaling	Yes	No	No
Index ranges	0 ≤ <i>h</i> ≤ 29	−12 ≤ <i>h</i> ≤ 12	−19 ≤ <i>h</i> ≤ 6
	0 ≤ <i>k</i> ≤ 29	−12 ≤ <i>k</i> ≤ 12	−19 ≤ <i>k</i> ≤ 18
	−20 ≤ <i>l</i> ≤ 27	−11 ≤ <i>l</i> ≤ 11	−17 ≤ <i>l</i> ≤ 17
Reflections collected	14 533	7636	12 064
Data/parameters	8605/224†		16 097/366
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0592		<i>R</i> (<i>F</i>) = 0.0281
	<i>wR</i> (<i>F</i> ²) = 0.1363		<i>wR</i> (<i>F</i> ²) = 0.0756
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0793		<i>R</i> (<i>F</i>) = 0.0299
	<i>wR</i> (<i>F</i> ²) = 0.1529		<i>wR</i> (<i>F</i> ²) = 0.0779
GOF <i>F</i> ² obs/all	1.562/1.477		1.052/1.071
Weight	1/(σ ² (<i>F</i> _o ²) + (0.05 <i>P</i>) ²)		{1/(σ ² (<i>F</i> _o ²) + (0.040 <i>P</i>) ² + 5.60 <i>P</i>)}
		{ <i>P</i> = (max(<i>F</i> _o ² , 0) + 2 <i>F</i> _c ²)/3}	

† Only reflections up to 2θ = 65° included.

Table 2. Averaging statistics corresponding to the different descriptions tried on the data from crystal (1)

$R_1(\text{int}) = \sum |I - \langle I \rangle| / \sum |I|$, $R_w(\text{int}) = \{ \sum [w(I - \langle I \rangle)^2] / \sum (wI^2) \}^{1/2}$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. N_{obs} is the number of space group allowed observations. N_{ind} is the number of independent observations. N_{param} is the number of parameters in the refinement.

Space group	Point group	<i>R</i> ₁ (int)	<i>R</i> _w (int)	<i>N</i> _{obs}	<i>N</i> _{ind}	<i>R</i>	<i>R</i> _w (<i>F</i> ²)	<i>N</i> _{param}
<i>P</i> 4 ₂ / <i>mnm</i>	4/ <i>mmm</i>	0.026	0.047	4366	1703	0.197	0.428	63
<i>P</i> 4 ₁ 2 ₁ 2	422	0.027	0.051	14508	11456	0.187	0.454	84
<i>P</i> 2 ₁ 2 ₁ 2 ₁	222	0.009	0.023	14517	13510	0.137	0.244	153

0*k*0, *k* = 2*n* + 1; 00*l*, *l* = 2*n* + 1) were systematically absent.

For crystal (1) averaging was performed in different point groups. The averaging seemed to be somewhat better in an orthorhombic symmetry, but tetragonal symmetry could not be excluded. The results are summarized in Table 2.

3.2. Structure determination

The only tetragonal space group fulfilling the conditions for the systematically absent reflections is *P*4₂2₁2. It was, however, not possible to solve the structure in this space group. Therefore, we turned to the previously published space groups, *P*4₂/*mnm* and *P*4₁2₁2. The structural model in space group *P*4₂/*mnm*, published by Veal *et al.* (1973), has the bridging oxygen placed on

(*mm*) symmetry and the Cr atoms placed on a crystallographic mirror plane. All structure refinements were performed using *SHELXL93* (Sheldrick, 1993). We attempted to see if the Veal *et al.* (1973) model could fit our data using only reflections with even *l* on the data from crystal (1). Our best solution had a final *R* value of *R*(*F*) = 0.1971 for all 3466 data (see Table 2). The results are illustrated in Fig. 1(a). Apart from the high displacement parameters of the cation, there is disorder of the water molecules and the chloride ions. Attempts to make a description in a superspace group with a commensurate modulation vector of *q* = *c*^{*}/2 were unsuccessful. Our next step was to insert the model into space group *P*4₁2₁2, suggested by Urushiyama, Nomura & Nakahara (1970), where two half molecules are found per asymmetric unit. The bridging O atoms lie either on a twofold axis perpendicular to the *c* axis or are disordered.

The result was a final R value of 0.1874 for all 5439 data (see Table 2). The resulting model had disordered water molecules and chloride ions and, as illustrated in Figs. 1(b) and 1(c), the hydroxo group of one of the two cations in the asymmetric unit was disordered.

The conclusion was that a satisfactory description could not be obtained in either of the two tetragonal space groups. Nevertheless, the structures found were not completely incorrect, as indicated by the R factors, and it was therefore obvious to look for a subgroup of $P4_12_12$. One of these, $P2_12_12_1$, actually fulfills the conditions for systematic absences and was therefore tried first. Lowering the symmetry from tetragonal $P4_12_12$ to orthorhombic $P2_12_12_1$ gave a much better result. The R value decreased immediately to 0.1366 for all 7232 reflections. An orthorhombic crystal structure with identical a and b cell parameters may emulate tetragonal symmetry by a rotation and/or reflection twin which would superimpose the (hkl) reflections with the $(k\bar{h}l)$ and/or $(\bar{k}hl)$ reflections

for the other twin individual. This is, for example, the case in many high T_c superconductors (McIntyre, Renault & Collin, 1988). Introducing a reflection twin in the (110) plane and refining the structure with anisotropic thermal parameters on Cr and Cl sites reduced the R value to 0.0735 for 8605 data. Within the standard uncertainties the two twin components appeared to be present in equal amounts – in agreement with the fact that the orthorhombic crystal emulates tetragonal symmetry. The model obtained in the orthorhombic space group is without any disorder. It was not possible to locate any H atoms, nor was it possible to use anisotropic displacement parameters on other atoms but those just mentioned. We assigned this to the twinned nature of the crystal.

3.3. Structure refinement

We turned our attention to crystal (2) for which we had collected a full sphere of data to $2\theta = 32^\circ$. Due to the limited resolution it was not possible to refine Cr and Cl atoms with anisotropic displacement parameters and likewise it gave problems to refine the N atoms with independent displacement parameters. Therefore, data were recollected as already described and the two data sets for crystal (2) were merged and averaged in point group 1. Using these data we were able to refine all non-H atoms with anisotropic displacement parameters. Maxima appeared in the difference electron density map at the expected hydrogen positions. However, for one of the water O atoms, O3, only one H atom could be localized. The H atoms attached to nitrogen were introduced in idealized geometry and the positions of all other H atoms were not refined. The thermal parameters of the H atoms were made equal to U_{eq} of the parent N or O atom multiplied by 1.5.

Analysis of the refinement of different twin models lead us to the conclusion that the best description of the twinning is a combined rotation and inversion twin. The subsequent refinement gave the following population parameters for the individuals that compose the macroscopic crystal: 0.13 (2) for the basis crystal, 0.37 (2) for the rotation twin, 0.37 (2) for the inversion twin and 0.13 (2) for the combined rotation and inversion twin. This means that the measured intensity of reflection hkl was composed of $0.13(2)I(hkl) + 0.37(2)I(\bar{k}hl) + 0.37(2)I(h\bar{k}l) + 0.13(2)I(\bar{k}\bar{h}l)$.

The positions of the Cr atoms conform to a higher symmetry than the other atoms. They may be described in space group $P4_2/mnm$ with $a = 16.160$, $c = 7.383$ Å. This centrosymmetric arrangement of the atoms with the most significant anomalous scattering contribution initially disturbed the calculation of the correct proportion of twin individuals [expressed as a warning in *SHELXL93* (Sheldrick, 1993), due to a Flack parameter with a very large standard uncertainty, $x = 0.3$, e.s.d. 0.5 (Flack, 1983)]. We overcame this problem realizing that

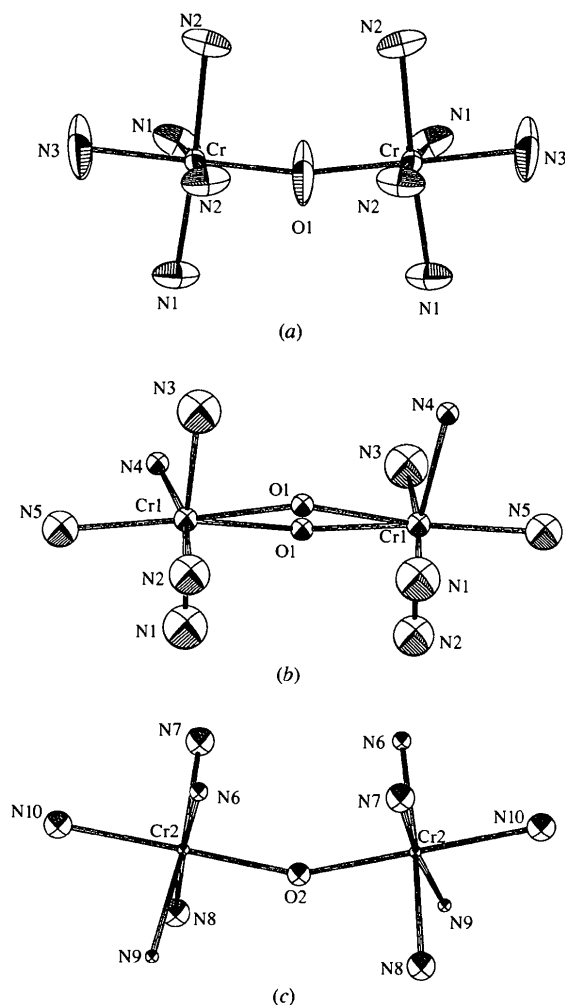


Fig. 1. ORTEPII (Johnson, 1976) 50% probability density plots of the cations in (a) $P4_2/mnm$, (b) and (c) $P4_12_12$.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU^j a_i^* \cdot a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr1	-0.49240 (4)	-0.07354 (4)	0.12810 (5)	0.00802 (14)
O1	-0.38882 (15)	-0.13921 (16)	0.12005 (15)	0.0106 (4)
N11	-0.5352 (3)	-0.1443 (3)	0.2345 (3)	0.0128 (9)
N12	-0.5519 (2)	-0.1476 (2)	0.0345 (3)	0.0126 (8)
N13	-0.4563 (2)	0.0030 (3)	0.0224 (3)	0.0122 (9)
N14	-0.4338 (2)	0.0044 (3)	0.2196 (3)	0.0187 (10)
N10	-0.5986 (2)	-0.0022 (2)	0.1409 (3)	0.0195 (9)
Cr2	-0.32262 (4)	-0.24190 (4)	0.12140 (5)	0.00702 (16)
N22	-0.3989 (2)	-0.2967 (2)	0.0260 (3)	0.0142 (9)
N21	-0.3927 (3)	-0.2905 (3)	0.2266 (3)	0.0130 (9)
N24	-0.2424 (2)	-0.1928 (2)	0.2166 (2)	0.0146 (9)
N23	-0.2461 (2)	-0.1989 (3)	0.0186 (3)	0.0115 (9)
N20	-0.2511 (2)	-0.3482 (2)	0.1209 (2)	0.0213 (9)
Cr4	-0.48841 (4)	-0.07255 (4)	0.61506 (5)	0.00743 (15)
O2	-0.39936 (17)	-0.15596 (16)	0.58992 (13)	0.0097 (5)
N41	-0.5409 (2)	-0.1481 (3)	0.7139 (3)	0.0126 (9)
N44	-0.5657 (2)	-0.1272 (2)	0.5208 (3)	0.0115 (8)
N43	-0.4430 (2)	0.0083 (3)	0.5171 (2)	0.0107 (9)
N42	-0.4165 (2)	-0.0092 (2)	0.7061 (2)	0.0155 (8)
N40	-0.5797 (2)	0.0138 (2)	0.6434 (3)	0.0161 (8)
Cr3	-0.31839 (4)	-0.24191 (4)	0.62386 (5)	0.00834 (15)
N31	-0.3949 (3)	-0.2907 (3)	0.7236 (3)	0.0159 (10)
N32	-0.2589 (2)	-0.1654 (3)	0.7166 (2)	0.0145 (8)
N33	-0.2371 (2)	-0.1972 (3)	0.5269 (3)	0.0139 (10)
N30	-0.2332 (2)	-0.3346 (2)	0.6582 (2)	0.0229 (10)
N34	-0.3683 (2)	-0.3219 (2)	0.5289 (3)	0.0162 (9)
Cl1	0.23827 (6)	0.14383 (7)	0.13817 (8)	0.0160 (2)
Cl2	0.25187 (6)	0.13453 (7)	0.61968 (7)	0.0167 (2)
Cl3	0.39154 (7)	0.00186 (6)	0.86646 (9)	0.0178 (3)
Cl4	0.87511 (6)	0.13401 (7)	0.87958 (5)	0.01530 (18)
Cl5	0.54484 (6)	0.19640 (6)	0.09484 (6)	0.01643 (19)
Cl6	-0.25811 (5)	-0.00196 (5)	0.08677 (5)	0.01787 (16)
Cl7	0.05567 (6)	0.31394 (6)	0.36973 (7)	0.01487 (17)
Cl8	0.89180 (6)	0.13385 (7)	0.37824 (5)	0.01395 (17)
Cl9	0.41689 (6)	0.67628 (7)	0.14542 (6)	0.01681 (19)
Cl10	0.60776 (7)	0.50920 (6)	0.13465 (9)	0.0166 (2)
O3	0.56290 (18)	0.18023 (19)	0.87604 (17)	0.0218 (6)
O4	0.69496 (16)	0.05522 (17)	0.85920 (17)	0.0315 (6)

the Cr atoms only contribute to reflections having *l* even. The correct proportions of the twin individuals could therefore be calculated by refining the twinning using $l = 2n + 1$ reflections only. The resulting twin parameters were then introduced on the full data set giving a correct solution indicated by a Flack parameter with a small standard uncertainty ($x = 0.00$, e.s.d. 0.01).

The final *R* value is $R(F) = 0.0299$ for 16 097 data and $R(F) = 0.0281$ for 15 725 data having $F_o > 4\sigma(F_o)$. The atomic parameters from the final refinement are given in Table 3.† It is noteworthy that neither the chloride ions nor the water molecules display any signs of disorder in contrast to the previous structural descriptions.

† Lists of H-atom coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0375). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4. Description of the structure

The coordination of two crystallographically independent cations labelled as *A* and *B* are illustrated in Fig. 2. The figures and the bond lengths in Table 4 reveal some small differences between the two dimeric cations. These are most pronounced at the bridging hydroxo group and in the relative positions of the H atoms bonded to the ammonia ligands. The torsion angles N13—Cr1—O1—H1 and N23—Cr2—O1—H1 in cation *A* are 44.5 (1) and -42.0 (1)°, respectively; the equivalent angles in cation *B*, N33—Cr3—O2—H2 and N43—Cr4—O2—H2, are ~10° smaller at 33.7 (1) and -33.8 (1)°. These variations are not reflected in the bridging Cr—O—Cr angles, which are 154.9 (1) and 154.4 (1)° in the *A* and *B* cations, respectively.

Neither of the cations possess any non-crystallographic symmetry. In cation *A* it is the relative orientation of H atoms in the ammonia groups N10, N20, N14 and N24 that deviates from the possible mirror plane symmetry; in cation *B* only ammonia groups N30 and N40 break the mirror plane symmetry. The four Cr—O distances fall in the range 1.973 (3)–2.006 (3) Å and the Cr—NH₃ bonds show variations from 2.051 (4) to 2.096 (3) Å.

The difference observed for the bridging hydroxo group can be explained by differences in their hydrogen-

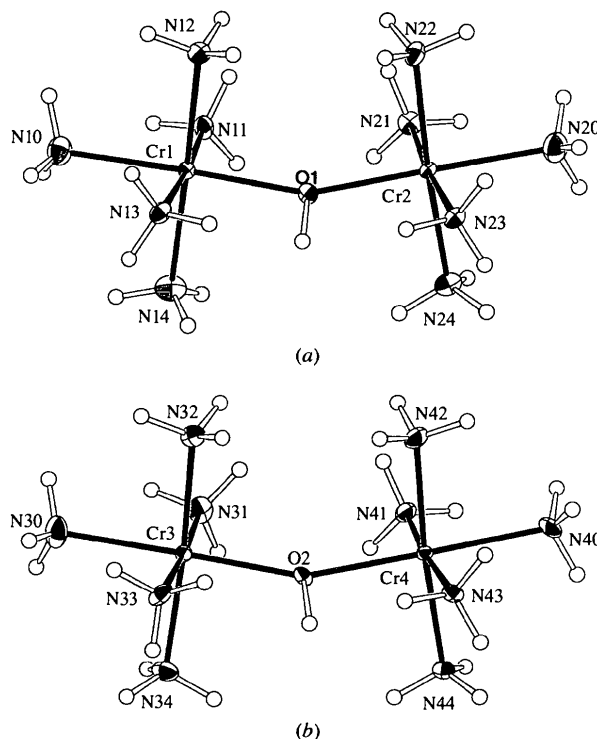


Fig. 2. ORTEPII (Johnson, 1976) 50% probability density plots of the two different cations in the asymmetric unit. H atoms are drawn as spheres with a fixed radius.

Table 4. Selected geometric parameters (Å, °) for the two cations

Cation A		Cation B	
Cr1—O1	1.985 (3)	Cr3—O2	1.973 (3)
Cr1—N10	2.077 (3)	Cr3—N30	2.096 (3)
Cr1—N11	2.062 (4)	Cr3—N31	2.078 (4)
Cr1—N12	2.066 (4)	Cr3—N32	2.080 (4)
Cr1—N13	2.076 (4)	Cr3—N33	2.073 (4)
Cr1—N14	2.076 (4)	Cr3—N34	2.072 (4)
Cr2—O1	1.975 (3)	Cr4—O2	2.006 (3)
Cr2—N20	2.071 (3)	Cr4—N40	2.073 (3)
Cr2—N21	2.077 (4)	Cr4—N41	2.083 (4)
Cr2—N22	2.070 (4)	Cr4—N42	2.051 (4)
Cr2—N23	2.078 (4)	Cr4—N43	2.082 (4)
Cr2—N24	2.070 (4)	Cr4—N44	2.069 (4)
Cr1—O1—Cr2	154.88 (10)	Cr3—O2—Cr4	154.38 (11)
O1—Cr1—N10	177.65 (13)	O2—Cr4—N40	179.00 (13)
O1—Cr1—N11	91.82 (13)	O2—Cr4—N41	91.60 (13)
O1—Cr1—N12	92.44 (12)	O2—Cr4—N42	92.92 (12)
O1—Cr1—N13	92.11 (13)	O2—Cr4—N43	92.32 (13)
O1—Cr1—N14	88.81 (13)	O2—Cr4—N44	91.23 (11)
N10—Cr1—N11	87.8 (2)	N40—Cr4—N41	87.9 (2)
N10—Cr1—N12	89.9 (2)	N40—Cr4—N42	86.2 (2)
N10—Cr1—N13	88.3 (2)	N40—Cr4—N43	88.2 (2)
N10—Cr1—N14	88.9 (2)	N40—Cr4—N44	89.63 (14)
N11—Cr1—N12	91.9 (2)	N41—Cr4—N42	93.7 (2)
N11—Cr1—N13	176.0 (2)	N41—Cr4—N43	176.04 (14)
N11—Cr1—N14	89.6 (2)	N41—Cr4—N44	88.6 (2)
N12—Cr1—N13	88.4 (2)	N42—Cr4—N43	86.7 (2)
N12—Cr1—N14	178.0 (2)	N42—Cr4—N44	175.2 (2)
N13—Cr1—N14	90.0 (2)	N43—Cr4—N44	90.8 (2)
O1—Cr2—N20	178.64 (13)	O2—Cr3—N30	179.00 (13)
O1—Cr2—N21	91.73 (13)	O2—Cr3—N31	93.04 (13)
O1—Cr2—N22	91.72 (12)	O2—Cr3—N32	93.17 (13)
O1—Cr2—N23	91.95 (14)	O2—Cr3—N33	89.95 (13)
O1—Cr2—N24	91.35 (12)	O2—Cr3—N34	90.54 (11)
N20—Cr2—N21	89.6 (2)	N30—Cr3—N31	87.0 (2)
N20—Cr2—N22	88.6 (2)	N30—Cr3—N32	87.8 (2)
N20—Cr2—N23	86.7 (2)	N30—Cr3—N33	90.0 (2)
N20—Cr2—N24	88.4 (2)	N30—Cr3—N34	88.5 (2)
N21—Cr2—N22	91.3 (2)	N31—Cr3—N32	91.9 (2)
N21—Cr2—N23	176.1 (2)	N31—Cr3—N33	177.0 (2)
N21—Cr2—N24	88.8 (2)	N31—Cr3—N34	90.7 (2)
N22—Cr2—N23	90.0 (2)	N32—Cr3—N33	87.4 (2)
N22—Cr2—N24	176.9 (2)	N32—Cr3—N34	175.37 (14)
N23—Cr2—N24	89.7 (2)	N33—Cr3—N34	89.8 (2)

bond interactions (*vide infra*), but the variations in Cr—N bonds lengths cannot be rationalized in terms of differences in their hydrogen bonding. The two octahedral coordination polyhedra in the cations are tilted slightly in an identical way relative to each other. The interplanar angle between the two planar entities in the A cation (O1 Cr1 N11 N10 N13) and (O1 Cr2 N21 N20 N23) is 14.8 (2)°, which is almost identical to the equivalent interplanar angle in the B cation, 15.0 (1)°.

Many other known salts of dimeric chromium(III) ammonia complexes form crystals where the cation is found on crystallographic symmetry elements. This is the case for the basic rhodo complex in μ -oxo-bis[pentaamminechromium(III)] chloride monohydrate (Urushiyama, 1972), where a crystallographic inversion centre relates

the two halves of the cation. The di- μ -hydroxo-bis[tetraamminechromium(III)] also possesses inversion symmetry both in its dithionate and chloride salts (Cline, Hodgson, Kallesøe, Larsen & Pedersen, 1983). It is remarkable that the completely equivalent compound μ -hydroxo-bis[pentaamminechromium(III)] chloride dihydrate, which differs from the present compound only by an additional water molecule, crystallizes with the cation on a crystallographic twofold axis (Engel & Güdel, 1977).

The coordination of the Cr atoms in these structures displays the same variations in Cr—O and Cr—N bond lengths as we found in the acid rhodo complex. The most significant structural difference between the μ -hydroxo-bis[pentaamminechromium(III)] cation in the dihydrate and in the present structure is the Cr—O—Cr angle, which is larger, 158.4 (7)°, in the dihydrate. The Cr—O and Cr—N distances compare well within experimental accuracy. The Cr—Cr distances in the present structure [3.8638 (14) and 3.8789 (15) Å] are also similar to that found in the dihydrate [3.878 (2) Å]. This is significantly larger than the Cr—Cr distance in the di- μ -hydroxo complexes, where a typical value is 3.023 (1) Å for bis(μ -hydroxo)bis[tetraamminechromium(III)] chloride tetrahydrate (Cline, Hodgson, Kallesøe, Larsen & Pedersen, 1983).

4.1. Crystal packing

It is likely that the small variations in coordination geometry around the chromium ion are due to differences in the intermolecular interactions. Among these, hydrogen bonds would be expected to play an important role. Each dimeric cation possesses 31 H atoms that could take part in hydrogen bonds. Including the protons from the water molecules there are 66 protons in the asymmetric unit that can be expected to take part in hydrogen bonds. In addition to the water molecules the potential acceptor atoms are the ten chloride ions. Needless to say, this can only lead to a very complex hydrogen-bond pattern.

Hydrogen bonds were selected so that for N—H...Cl bonds the H...Cl distance was smaller than 3.0 Å and for N—H...O bonds the H...O distance was smaller than 2.6 Å. The angle for bifurcated hydrogen bonds should lie between 110 and 130° and the angle for single hydrogen bonds should be greater than 140°.†

An analysis of the intermolecular interactions in the crystals showed that apart from two H atoms bonded to N10 and N30 (Fig. 2) and the missing H atom of O3, all H atoms that were expected to be involved in hydrogen bonds are indeed doing so. Most of these are of the usual linear two-centre type but, as shown in Fig. 3, several three-centre (bifurcated) hydrogen bonds are also formed. The N—H...Cl distances are between 3.242 (5) and 3.697 (4) Å and the N—H...O distances are 3.097 (6),

† All hydrogen-bond geometries have been deposited.

3.123 (6) and 3.157 (4) Å. The O—H...O distance for the O1—H1O...Cl6 bond is 3.102 (3) Å and for the O2—H2O...Cl4 bond 3.151 (2) Å. We will not attempt a complete description of the hydrogen bonds, but rather highlight some significant features.

The two dimeric cations are surrounded by chloride ions and water molecules, as illustrated by the stereopairs in Fig. 3. These drawings show that cation *A* is hydrogen bonded to 13 chloride ions and one water molecule, whereas 14 chloride ions and one water molecule surround cation *B*. Cl16 and Cl18 make equivalent hydrogen bonds to cations *A* and *B*, respectively, two two-centre (linear) and two three-centre (bifurcated). The hydrogen bonds formed from cation *A* to Cl19, Cl12 and Cl17 are equivalent to those between cation *B* and Cl18,

Table 5. Number of hydrogen bonds from the hydrogen-bond acceptors to the two dimers, respectively

Anion	Dimer <i>A</i>	Dimer <i>B</i>
Cl1	3	4
Cl2	5	3
Cl3	2	4
Cl4	4	3
Cl5	1	3
Cl6	4	4
Cl7	2	3
Cl8	4	4
Cl9	5	1
Cl10	4	2
O3	0	2
O4	1	0

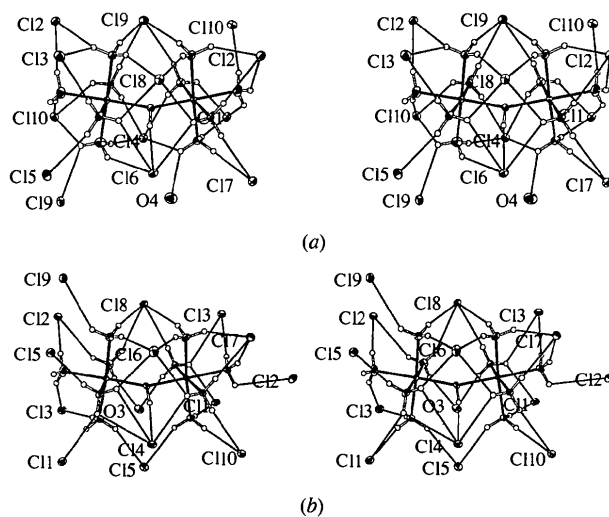


Fig. 3. ORTEPII (Johnson, 1976) stereoplot of the hydrogen-bonding patterns of the two different cations in the asymmetric unit. The orientations of the two cations are identical to the orientation in Fig. 2. The thermal ellipsoids enclose 50% probability, the H atoms are drawn as spheres with a fixed radius.

Cl17 and Cl10. The bridging hydroxo groups are hydrogen bonded to a chloride ion in both cations Cl16 and Cl14, it could be the different hydrogen-bond interactions of these ions that give rise to the differences in the conformation of the bridging hydroxo group.

It is apparent from Fig. 3 that there are also differences in the environments of the two cations. This is quite pronounced in the way the two water molecules are interacting with the cation. In cation *B* water molecule O3 accepts protons from two of the ammonia groups and is thereby part of its immediate environment. In contrast we note that O4 appears to be interacting less tightly with cation *A* through a single hydrogen bond. The two water molecules are connected by the hydrogen bond O3—H...O4, which serves as one of the links between the two cations. From Fig. 3, it is obvious that several of the chloride ions play the same role. The different chloride ions are acceptors for four to eight hydrogen bonds made to the neighbouring cation. The variations in these interactions are illustrated in Table 5.

An ORTEP (Johnson, 1976) drawing illustrating the packing of the crystal structure is shown in Fig. 4. An analysis of the geometry using the program PLATON

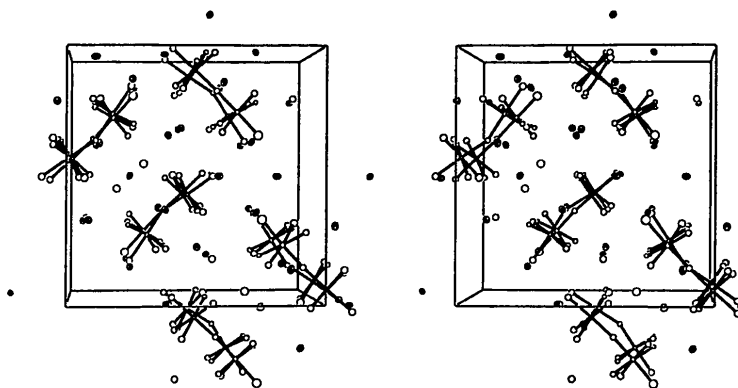


Fig. 4. ORTEPII (Johnson, 1976) stereopair illustrating the packing of the acid rhodo complex viewed along the *c* axis. The *a* axis is horizontal and the *b* axis is vertical. The shaded spheres represent the chloride ions.

(Spek, 1990) shows that the angle between the two planes defined by Cr1, O1 and Cr2 and the $(-x + \frac{1}{2}, -y, z + \frac{1}{2})$ symmetry equivalent of Cr3, O2 and Cr4, respectively, is 87.1 (3)°. The plane defined by Cr1, O1 and Cr2 is almost perpendicular to the *c* axis, while the plane defined by Cr3, O2 and Cr4 is approximately parallel to the *c* axis. This is in excellent agreement with results from polarized absorption spectroscopy and Zeeman experiments by Riesen & Güdel (1986). Their results were interpreted in terms of two different dimers in the unit cell and the angles between the Cr—O—Cr planes and the *c* axis were found to be 0 ± 10 and $90 \pm 10^\circ$, respectively.

We may then establish that the dimer referred to as *A* by Riesen & Güdel (1986) is identical to our cation *B* (defined by Cr3 and Cr4) and the dimer referred to as *B* is identical to our cation *A* (defined by Cr1 and Cr2).

5. Conclusions

This new crystal structure determination for the acid rhodo complex may explain the spectroscopic and magnetic properties of the crystals. The two dimeric cations have identical geometry which corresponds closely to the geometry of the cation in the equivalent dihydrate. This provides further indication of the soundness of the model for the monohydrated salt.

The present structure determination has shown that simple compounds can form very complex crystal structures that can be quite difficult to determine. This structure determination gave the experience that to resolve fairly complicated twinning such as that we have encountered in the acid rhodo complex it is essential to base the refinement on independent measurements of symmetry-related reflections and maintain these as individual reflections. In the present case it turned out to be important to have half a sphere of reflection data instead of just a quarter of a sphere of reflection data.

The difficulties of the structure determination of the acid rhodo complex must be assigned to the unusual symmetry of the crystal structure. First, the crystal symmetry is actually orthorhombic, but due to twinning the diffraction pattern displays tetragonal symmetry. Secondly, the arrangement of the Cr atoms, dominating in the diffraction pattern, corresponds to centrosymmetric

tetragonal symmetry of a smaller cell (having *c*/2). To break this pseudo-symmetry of the structure it is important that also the weak reflections have been measured accurately.

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